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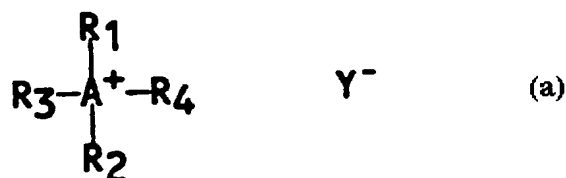
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<p>(21) International Application Number: PCT/EP96/01732 (22) International Filing Date: 24 April 1996 (24.04.96) (30) Priority Data: 95201067.6 25 April 1995 (25.04.95) EP (34) Countries for which the regional or international application was filed: GB et al. (71) Applicant (for all designated States except CA): SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL). (71) Applicant (for CA only): SHELL CANADA LIMITED [CA/CA]; 400 - 4th Avenue S.W., Calgary, Alberta T2P 2H5 (CA). (72) Inventors: KLOMP, Ulfert, Cornelis; Badhuisweg 3, NL-1031 CM Amsterdam (NL). REIJNHART, Rene; Badhuisweg 3, NL-1031 CM Amsterdam (NL).</p>		<p>(81) Designated States: AU, BR, CA, CN, MX, NO, NZ, VN, Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>

(54) Title: METHOD FOR INHIBITING THE PLUGGING OF CONDUITS BY GAS HYDRATES

(57) Abstract

A method for inhibiting the plugging of a conduit by gas hydrates comprises adding to a mixture of water and hydrocarbons flowing through the conduit an amount of a hydrate formation inhibitor component of formula (a), wherein two of R₁-R₄ are independently normal or branched alkyls having 4 or 5 carbon atoms, two of R₁-R₄ are independently representing organic moieties having at least 8 carbon atoms, A represents a nitrogen or phosphorus atom, and Y represents an anion.



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METHOD FOR INHIBITING THE PLUGGING OF
CONDUITS BY GAS HYDRATES

This invention relates to a method for inhibiting the plugging by gas hydrates of conduits containing a mixture of low-boiling hydrocarbons and water.

Low-boiling hydrocarbons, such as methane, ethane, propane, butane and iso-butane, are present in natural gas and also in crude oil. Because water may also be present in varying amounts in natural gas and crude oil, the mixture, under conditions of elevated pressure and reduced temperature, tends to form gas hydrate crystals. Gas hydrates are clathrates (inclusion compounds) of gases in a lattice consisting of water molecules. The maximum temperature at which gas hydrates can be formed strongly depends on the pressure of the system. For example, ethane at a pressure of approximately 1MPa can form hydrates only at temperatures below 4 °C whereas at a pressure of 3MPa stable hydrates can be present at temperatures as high as 14 °C. With respect to this strong dependence of the hydrate melting point on pressure, hydrates markedly differ from ice.

As described by M. von Stackelberg and H.R. Muller (Z. Electrochem., 58, 25 (1954)), methane and ethane hydrates form cubic lattices having a lattice constant of 1.2 nm (hydrate structure I). The lattice constant of the cubic propane and butane gas hydrates is 1.73 nm (hydrate structure II). However, the presence of even small amounts of propane in a mixture of low-boiling hydrocarbons will result in the formation of gas hydrates having structure II (J.H. van der Waals and J.C. Platteeuw, Adv. Chem. Phys. 2, 1 (1959)).

It has been known for a long time, that gas hydrate crystals, when allowed to form and grow inside a conduit such as a pipeline, tend to block or even damage the conduit. To prevent such blocking, the following measures are possible in principle: removal of free water; maintaining elevated temperatures and/or reduced pressures or the addition of melting point depressants (antifreezes). In practice, antifreezes are most frequently used. However, antifreezes, such as the lower alcohols and glycols, have to be added in substantial amounts to be effective, typically several tens of percent by weight of the water present. A disadvantage of such amounts is the cost of the antifreeze; a further disadvantage is that recovery is relatively expensive.

An attractive alternative to the anti-hydrate measures described above, particularly the antifreezes, is to use a crystal growth inhibitor. The principle of interfering with crystal growth is known.

Plants and poikilothermic animals such as insects and cold-water fish are known to protect themselves from freezing, both by antifreezes such as glycols and by special peptides and glycopeptides (termed antifreeze proteins and antifreeze glycoproteins) that interfere with ice crystal growth (A.L. de Vries, Comp. Biochem. Physiol, 73, 627 (1982)). Although we found such cold-water fish peptides and glycopeptides to be effective in interfering with the growth of gas-hydrate crystals, their production and use for this purpose are currently considered to be uneconomical.

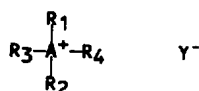
In International Patent Application Publication WO 93/25798 the use of polymers and copolymers of N-vinyl-2-pyrrolidone for inhibiting the formation, growth and/or agglomeration of gas hydrate crystals is disclosed.

It is therefore an object of the present invention to provide a method to inhibit formation of hydrates in streams containing at least some light hydrocarbons and water. It is a further object to provide such a method wherein a high concentration of additive is not required.

It has now been found that certain alkylated ammonium or phosphonium compounds are very effective, at relatively low concentrations, in interfering with the growth of gas hydrate crystals. These compounds can therefore be very useful in inhibiting the plugging by gas hydrates of conduits containing low-boiling hydrocarbons and water. The subject compounds have four organic groups in their molecule, of which two have at least eight carbon atoms.

These and other objects are therefore accomplished by a method for inhibiting the plugging of a conduit, the conduit containing a flowing mixture comprising an amount of hydrocarbons having from one to eight carbons and an amount of water wherein the amounts of hydrocarbons and water could form hydrates at conduit temperatures and pressures, the method comprising the steps of:

adding to the mixture an amount of a hydrate formation inhibitor component of the formula



wherein two of R_1 - R_4 are independently

normal or branched alkyls having 4 or 5 carbon atoms, two of R_1 - R_4 are independently representing organic moieties having at least eight carbon atoms,

A represents a nitrogen or phosphorus atom, and

Y represents an anion;

the amount of the hydrate formation inhibitor compound being effective to inhibit formation of hydrates in the mixture at conduit temperatures and pressures; and flowing the mixture containing the hydrate formation inhibitor through the conduit.

Preferably, two of R_1 - R_4 independently contain between 8 and 20 carbon atoms, advantageously in the range 10 to 16 carbon atoms. Suitably, compounds are used wherein two of R_1 - R_4 contain the same number of carbon atoms, each being at least 8. Preferably, use can be made of components wherein two of R_1 - R_4 represent cocoyl moieties (i.e. the alkyl chains present in coconut fatty acids or similar compounds).

Suitably, at least one of R_1 - R_4 contains at least a hetero-atom in addition to at least 8 carbon atoms. Suitable hetero-atoms comprise oxygen, nitrogen and sulphur, preferably oxygen or nitrogen. The groups R_1 - R_4 comprising at least 8 carbon atoms suitably represent alkyl, alkenyl, aryl, arylalkyl, arylalkenyl, alkylaryl, alkenylaryl and glycol moieties.

Preferred ammonium or phosphonium alkylated compounds according to the invention are those wherein two of R_1 - R_4 independently represent a $-(CH_2-CHR_5-O-)_nH$ or $-(CH_2-CHR_5-N-R_6)_mCH_2-CH_3$ moiety wherein R_5 represents H or CH_3 , R_6 represents H or alkyl, such as CH_3 or C_2H_5 , n represents an integer from 4 to 50 and m represents an integer from 3-5.

Further preferred hydrate formation inhibition compounds are those ammonium or phosphonium alkylated compounds according to the invention wherein at least one of R_1 - R_4 represents a

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$-(CH_2-CHR_5-O)_p-(CHR_5)_q-O-C-R_7$ moiety, wherein R_5 represents H or CH_3 , p represents 0 or an integer up to

50, q represents an integer up to 20 and R₇ represents an alkyl, alkenyl, aryl, arylalkyl, arylalkenyl, alkylaryl or alkenylaryl group having at least a carbon chain of 6 atoms.

5 Compounds which can be used advantageously are those wherein q represents 2-4 and R₇ represents an alkyl or alkenyl group having at least 9 carbon atoms or compounds wherein p is zero, q represents 2 and R₇ represents an alkyl or alkenyl group of between 9 and 18 carbon atoms.
10 Preferred compounds are those wherein two of R₁-R₄ represent the same ester moiety. Examples of such preferred compounds are those wherein R₇ represents the carbon chain of coconut fatty acid or tallow fatty acid.

15 Suitably, the anion (Y⁻) represents a hydroxide, a carboxylate, a halide such as chloride or bromide, a sulphate or an organic sulphonate. Preferably, Y⁻ represents a chloride, bromide or a sulphate.

20 The compounds containing oxygen and/or nitrogen atoms as defined hereinbefore are advantageous in that they have biodegradable properties which renders them eminently suitable for the envisaged use. A further advantage in the envisaged use is that such compounds are sparingly soluble in water which allows discarding production water containing only marginal concentrations
25 of such compounds.

30 The alkylated compounds according to the invention can be chemically bound through one of the R₁-R₄ groups to polymers. They then are branches of these polymers. Examples of polymers to which the alkylated compounds according to the invention can be suitably bound include polyacrylic acid, and polymers and copolymers of N-vinyl-2-pyrrolidone.

35 If desired, corrosion inhibitors may be added to the hydrocarbon/water mixture. Corrosion inhibitors known to those skilled in the art can be suitably applied.

Suitable corrosion inhibitors comprise primary, secondary or tertiary amines or quaternary ammonium salts, preferably amines or salts containing at least one hydrophobic group.

5 Examples of corrosion inhibitors comprise benzalkonium halides, preferably benzyl hexyldimethyl ammonium chloride.

Fig. 1 is a schematic drawing of the apparatus used in the experimental set-up.

10 The amount of the alkylated compound used in the process according to the invention is generally between 0.05 and 11 wt%, preferably between 0.1 and 5 wt%, most preferably between 0.1 and 0.5 wt%, based on the amount of water in the hydrocarbon-containing mixture.

15 The alkylated compounds according to the invention can be prepared in manners which are known in the art, from ingredients which are simple and abundantly available.

20 The alkylated compounds according to the invention can be added to the subject mixture of low-boiling hydrocarbons and water as their dry powder or, preferably, in concentrated solution.

25 The alkylated compounds according to the present invention can be used together with a polymer of an ethylenically unsaturated N-heterocyclic carbonyl compound, suitably an aliphatic (N-heterocyclic carbonyl) polymer with units derived from N-vinyl-pyrrolid-2-one and an unsaturated hydrocarbon having between 4 and 30 carbon atoms. Suitably, the polymer unit is derived from N-vinyl-pyrrolid-2-one and butylene, octylene, 30 dodecylene, hexadecylene, eicosylene and tricosylene. Reference is made to the polymers or copolymers of N-vinyl-2-pyrrolidone which are the subject of the aforementioned International Patent Application Publication 35 WO 93/25798, and the combined effect is at least

additive. The polymers or copolymers of N-vinyl-2-pyrrolidone are preferably added to an amount of between 0.05 and 4 wt%, based on the water content.

The compounds may further be combined with film-forming agents which are known to prevent water-wetting of metal surfaces and to interfere with the agglomeration of any crystallites and with their adhesion to the wall of the conduit through which the mixture is passed.

Typical examples of such film-forming agents are long-chain alkyl amines, alkyl diamines, quaternary ammonium salts and imidazolines, optionally in combination with high molecular-weight organic acids. Mono-valent and divalent salts of long-chain alkaryl sulphonic acids are also suitable as film-forming agents. These salts are disclosed in European Patent Specification No. 457,375.

The following Examples will illustrate the invention.
Description of equipment.

In the type A and B experiments that are detailed below field conditions were simulated by using a high-pressure flow loop facility which is schematically shown in Figure 1 and which consists of a stainless steel pipeloop (2a-c) having an inner diameter of 19 mm and an effective length of 108 metres, a mixing tank (1) and a gear pump (3) for circulating a hydrate forming mixture of water and liquid hydrocarbons through the loop. The pipeloop can be seen as being divided into 9 sections (each having a length of 12 metres) and each of which is equipped with a thermometer and a differential pressure meter allowing the monitoring of the pressure drop over each individual section.

Sections 1-6 (2a) and section 9 (2c) are surrounded by a coaxial pipe through which a temperature-controlled liquid is circulated in counterflow to the hydrate forming medium (which flows from section 1 to section 9).

Sections 7 and 8 (2b) are thermally well-insulated and equipped with viewing windows (mounted near the inlet of section 7 (4a) and the outlet of section 8(4b)) to allow the visual observation of the hydrate forming medium in the pipelooop.

Hydrate formation is triggered by cooling 1 cm² of the inner surface of the pipelooop near the end of section 3 to a constant temperature of -15 °C. This "cold spot" was switched-off immediately after the first hydrates were formed.

Standard filling and pre-conditioning procedure.

In all type A and B experiments described hereafter, the loop facility (having a total volume 62.5 litres) was (at a temperature of 24 °C) initially filled with 5 litres of water, 39.2 litres of a hydrocarbon liquid, such as "SHELLSOL D60" (trade name for a mixture of paraffinic and naphthenic hydrocarbons, mainly in the C₁₀ - C₁₂ range, available from Shell Oil Company, Houston, Texas) and 3.2 kilograms of propane.

Subsequently, methane was introduced until the equilibrium pressure of the system was 78 bara. This procedure leads to the formation of a three-phase system (i.e. a vapour phase, a liquid aqueous phase and a liquid hydrocarbon phase) in which can form stable hydrates at temperatures below 19 °C. In all type A and B experiments the liquid phases of the hydrate forming medium were circulated through the pipelooop at a rate of 120 grams/second (or 540 litres per hour) which corresponds to a Reynolds number of approximately 8000 (turbulent flow). Prior to the start of each experiment the hydrate forming medium was circulated for approximately one day at a temperature of 23 °C to obtain thermodynamic equilibration and an even distribution of the liquid phases throughout the entire system.

The effect of an additive (hydrate formation inhibitor component) was assessed by comparing the experimental results of a blank test (in which no additive had been added to the hydrate forming medium) with those of an additive test (in which the system was doped with the additive concerned) and which was carried out under the same conditions of the blank test. Two different types of experiment viz. type A and B were performed to detect such effect.

TYPE A EXPERIMENTS

These experiments represent the hydrate remelting operation mode in which the hydrate forming medium is cooled exponentially in the first three sections of the flow loop.

Experiment A 1a (blank test)

During this experiment the loop was filled with 5 liters of water, 3.2 kilograms of propane and 39.2 liters of "SHELLSOL D60" (the trade name for a mixture of paraffinic and naphthenic hydrocarbons, mainly in the C₁₀-C₁₂ range, available from Shell Oil Company, Houston, Texas) and pressurised with methane until the equilibrium pressure at 24 °C was 78 bara. After performing the initial preparations described above, the experiment was started by gradually controlling the temperature of the coolant circulating around the first six sections in such a way that the hydrate forming liquids exited the sixth section at a temperature of 23-t °C in which t denotes the time (in hours) which elapsed since the start of the cooling. When passing through the ninth section the hydrate forming medium was reheated such that it always entered the first section at a fixed temperature of 23 °C. When applying this experimental procedure the temperature dropped exponentially from 23 to 23-t degrees over the first three sections, remained essentially constant in

sections 4 through 8, after which the medium was reheated in the ninth section. In this mode of operation the hydrate crystals which were formed in sections 1 to 8 but which were transported by the flow to the last section were all melted.

When this experiment was performed the pressure drop over the pipeloop started to increase after four hours (which was due to hydrate deposition at the pipeline wall) at which stage the medium reached a minimum temperature of 18.7 °C near the outlet of the sixth section. Hereafter the medium could be circulated for another hour during which the pressure drop was gradually increasing until it exceeded a value of 2 bara which was considered to correspond with a complete blockage of the loop. At this time the minimum temperature of the medium at the outlet of the sixth section was 17.9 °C.

Experiment A 1b

This experiment was identical to experiment A 1a except for the addition of 12.5 grams of dibutyl-dicocoylammonium bromide to the hydrate forming mixture. In this case the cooling cycle could be maintained for 22 hours at which stage the temperature of the medium had reached a minimum temperature of 1 °C whereas the pressure drop over the loop had only slightly increased. This increase was due to an increased viscosity of the hydrate forming medium rather than to hydrate deposition. Hereafter the circulation was maintained for one hour during which the temperature profile over the loop was kept constant and during which the pressure drop did not increase. Then the circulation was stopped for a few minutes during which a milky aqueous layer separated rapidly from the water/hydrocarbon mixture. Note that during the periods during which the circulation is stopped the hydrate forming medium residing in sections 1 through 8 rapidly attained a constant temperature which

corresponds to the lowest temperature (i.e. 1 °C in this particular experiment) which the hydrate forming medium had reached during the preceeding period of circulation. The original temperature profile over the loop was restored very shortly after the restart of the circulation. When the circulation was restarted larger chunks of hydrates were observed to have formed during the shut-in period. These chunks, which did not adhere onto the pipeline wall, jammed the loop a few minutes after the restart.

Experiment A 1c

This experiment was identical to experiment A 1b except that the cooling cycle was maintained for 13 hours until the medium reached a minimum temperature of 10 °C. Then the circulation was consecutively: stopped for 30 seconds, restarted for 10 minutes, stopped for 1 minute, restarted for 20 minutes, stopped for 5 minutes, restarted for 20 minutes, stopped for 30 minutes and restarted again. Each time the circulation could be smoothly restarted whereas the pressure drop did not increase with respect to the situation prior to shut-down.

During the following five hours the cooling cycle was continued until the hydrate forming medium reached a minimum temperature of 5 °C after which the sequence of shut-downs and restarts as described above was repeated. Again no pressure drop increase was observed and the circulation could be smoothly restarted after each shut-down period.

Then the cooling cycle was continued again for 4 hours until the medium reached, when exiting the sixth section, a minimum temperature of 1 °C which corresponds to the situation during experiment A 1b just prior to shut-down. The circulation was maintained for 14 hours during which the temperature profile over the loop was

held constant and no increase in pressure drop was observed. Hereafter the circulation was stopped for 5 minutes during which a liquid aqueous layer segregated from the hydrocarbon mixture. After a shut-down period of 1 minute hydrates were clearly seen to form at the interface between this layer and the hydrocarbon liquid. When the circulation was restarted the pressure drop had slightly increased with respect to the situation prior to shut-down. After 2.25 hours of circulation both the hydrates deposited and the water layer were completely resuspended in the hydrocarbon phase. Hereafter the circulation was stopped for 30 minutes during which a large amount of hydrates were formed. After restart of the circulation the pressure drop appeared to have increased significantly. The circulation could be maintained for 6.5 hours during which the pressure drop was steadily fluctuating. Whether this was due to a periodic (near) blocking of the loop by hydrates or by a fault in the differential pressure meters remains uncertain.

Experiment A 2a (blank test)

During this reference experiment the loop was filled with 5 liters of water, 3.2 kilograms of propane and 39.2 liters of a mixture containing 85 w% of SHELLSOL D60 and 15 w% of SHELLSOL R (the trade name for a mixture containing 80% of aromatic hydrocarbons, mainly in the C₁₀-C₁₂ range) and pressurised with methane until the equilibrium pressure at 24 °C was 78 bara. In the same way as described in experiments A 1a - A 1c the hydrate forming medium was cooled in such a way that the temperature at which the medium exited the sixth section decreased (starting from 23 °C) by 1 °C per hour. After 4.2 hours, at which time the minimum temperature of the medium was 18.8 °C, the pressure drop over the loop started to increase. The circulation and cooling could be

continued for another 1.4 hours (when the minimum temperature of the hydrate forming medium reached 17.4 °C) after which the loop became blocked by hydrates.

Experiment A 2b

5 This experiment was identical to experiment A 2a except for the addition of 12.5 grams of the diester of dibutyldiethanolammonium bromide and coconut fatty acid. The cooling cycle was continued for 22 hours at which
10 time the hydrate forming medium had reached a minimum temperature of 1 °C and the pressure drop over the loop had increased slightly due to an increase of the
 viscosity of the medium. Subsequently the circulation was, whilst keeping the temperature profile over the loop constant, maintained for another 3 hours during which the
15 pressure drop over the loop remained essentially constant. Hereafter the circulation was stopped for 1 hour and subsequently restarted. The circulation could be maintained for 3 hours before the loop became blocked by hydrates. During this period the pressure drop over
20 the loop was, compared to the situation prior to shut-down, increased by a factor of six indicating the deposition of hydrates at the pipeline wall.

Experiment A 2c

 This experiment was identical to experiment A 2b
25 except that after 22 hours of cooling (at the end of which the hydrate forming medium had attained a minimum temperature of 1 °C) the circulation was maintained for 65 hours whilst the temperature profile over the loop was kept constant. It appeared that the pressure drop over
30 the loop started to increase markedly after 8 hours of circulation. This continued for another 57 hours at which time the loop became completely blocked by hydrates.

Experiment A 2d

 Experiment A 2c was repeated except that the cooling
35 cycle was stopped after 18 hours at which time the

minimum temperature of the hydrate forming medium was 5 °C. Hereafter the temperature profile over the loop was kept constant whilst the hydrate forming medium was circulated for 4 hours during which time the pressure drop over the loop remained constant. Subsequently the circulation was stopped during 2.5 hours and then restarted. Large chunks of hydrates appeared to have formed during shut-down. These chunks of hydrates jammed the loop a few minutes after the circulation was restarted.

Experiment A 3a

This reference experiment was a duplicate of experiment A 2a. During this experiment the first increase in the pressure drop was observed when the minimum temperature of the medium was 20 °C and approximately one hour later the loop became completely blocked by hydrates when the minimum temperature of the medium was 18.9 °C.

Experiment A 3b

This experiment was identical to experiments A 2a and A 3a except for the addition of 12.5 grams of the diester of dibutyldiethanolammonium chloride and tallow fatty acid. The pressure drop over the loop started to increase during the cooling cycle when the minimum temperature of the hydrate forming medium was 7 °C and 2 hours later the loop became completely blocked by hydrates when this temperature was 5 °C.

Experiment A 3c

This experiment was identical to experiment A 3b except for the extra addition of 150 grams of NaCl and of 32.5 grams of the diester of dibutyldiethanol ammonium chloride and 2-ethylhexanoic acid. 24 hours after the cooling cycle was started the hydrate forming medium at the outlet of the sixth section had reached a temperature of -1 °C whereas the pressure drop over the loop had

increased slightly due to an increase in the viscosity of the hydrate forming medium. Hereafter the circulation was maintained for another 4 hours whilst the temperature profile over the loop was kept constant. The pressure drop over the loop did not increase during this period. Subsequently the circulation was stopped for 4.5 hours. Then the circulation could be restarted and the pressure drop over the loop appeared to be identical to the pressure drop prior to the shut-down period.

TYPE B EXPERIMENTS

These experiments represent the hydrate recirculation mode in which the temperature of the hydrate forming medium is kept constant throughout the entire test facility.

Experiment B 1a (blank test)

The test facility was filled with 5 liters of water, 3.2 kilograms of propane and 39.2 liters of SHELLSOL D60 after which methane was added until the equilibrium pressure at 24 °C was 78 bara (the same filling as the one used in experiment A 1a). After performing the initial preparations described above this reference experiment was started by cooling the hydrate forming medium at a rate of 1 °C/hr. Because no heating was applied in the ninth section, the temperature of the hydrate forming medium was independent of the position of the medium in the test facility. In this type of experiment the hydrates which are carried by the flow become severely crushed when they pass through the gear pumps. During this experiment the first increase in the pressure drop was observed after four hours by which time the temperature of the medium was 18.8 °C. The circulation could be maintained for another hour during which the pressure drop increased continuously until the loop became completely blocked by hydrates. At the time

of blocking the temperature of the hydrate forming medium was 18.0 °C.

Experiment B 1b

This experiment was identical to experiment B 1a except for the addition of 12.5 grams of dibutyl-dicocoylammonium bromide. Eleven hours after the start of the cooling cycle, at which time the temperature of the medium was 12 °C, the circulating liquids became hazy whereas the pressure in the system dropped rapidly indicating that a substantial amount of hydrates were formed. The cooling cycle was continued for another 11 hours after which the temperature of the hydrate forming medium was reduced to 1 °C and only a slight increase in the pressure drop over the loop was observed. The medium was circulated for another two hours during which the pressure drop did not increase. At this stage the pressure of the system had dropped to 52 bar indicating that practically all water was converted into hydrates. Subsequently the circulation was stopped resulting in the slow separation of a layer of very fine hydrate crystals from the hydrate forming medium. This shut-down condition was maintained for the next 22 hours during which the temperature of the medium was kept at 1 °C. When the circulation was restarted the layer of loose powder hydrates became readily resuspended into the hydrocarbon liquids resulting in the formation of the hydrate suspension which was observed prior to shut-down. Also the pressure drop over the pipelooop had not increased with respect to the situation before the circulation was stopped.

Experiment B 1c

This experiment was identical to experiment B 1b except that the hydrate forming medium was uniformly cooled at a rate of 25 °C per hour until (i.e. after 0.7 hours) the temperature of the medium was reduced to

1 °C. At this point the pressure of the system was 63 bar indicating that hardly any hydrates were formed. The circulation was maintained for another 16 hours during which the pressure drop did not increase significantly even though the system pressure decreased to 52 bar indicating that practically all water became converted into very fine powder hydrates. Next the circulation was stopped whilst the temperature of the medium was kept constant at 1 °C. After three hours of shut-down the circulation was restarted which again resulted in a rapid redispersion of the layer of powder hydrates into the liquid hydrocarbon phase. The pressure drop over the pipelooop had not increased with respect to the situation prior to shut-down.

Experiment B 1d

This experiment is identical to experiment B 1c in that the medium was rapidly cooled from 23 °C to 1 °C at a rate of 25 °C per hour after which the circulation was stopped immediately. At this time the system pressure was 63 bar indicating that little hydrates were formed. The flow could be smoothly restarted after a shut-down period of 1.5 hours when the system pressure was still 63 bar. The pressure drop over the loop had not increased compared to the situation prior to shut-down.

Experiment B 2a

In this experiment the loop was filled with 12.5 grams of the diester of dibutyldiethanol ammonium bromide and coconut fatty acid, 5 liters of water, 3.2 kilograms of propane, 39.2 liters of a mixture consisting of 85% SHELLSOL D60 and 15% of SHELLSOL R, after which methane was added until the equilibrium pressure of the system at 24 °C was 78 bara. (Note that this filling is identical to the one used during experiment 2b). The hydrate forming medium was uniformly cooled at a rate of 1 °C per hour during 22 hours until

the temperature of the medium was 1 °C. Then the circulation was continued for another hour whilst maintaining the temperature of the medium at 1 °C. Hereafter the flow was stopped causing fine powder hydrates to segregate from the hydrocarbon liquids. These powder hydrates were rapidly redispersed in the hydrocarbon liquid when the flow was restarted after 93 hours of shut-down. The pressure drop over the loop had not increased with respect to the situation prior to shut-down.

Experiment B 2b

In this experiment the loop was filled with 12.5 grams of the diester of dibutyldiethanol ammonium chloride and tallow fatty acid, 5 liters of water, 3.2 kilograms of propane, 39.2 liters of a mixture of 85% SHELLSOL D60 and 15% SHELLSOL R, after which methane was added until the equilibrium pressure of the system was 78 bara. The hydrate forming medium was uniformly cooled at a rate of 1 °C per hour until it reached a temperature of 1 °C. Hereafter the circulation was maintained for another hour during which the temperature of the medium was kept constant at 1 °C. Then the circulation was stopped during 3.5 hours which caused powder hydrates to segregate from the hydrocarbon liquid. These hydrates were readily redispersed in the hydrocarbon liquids when the flow was restarted after this shut-down period. The pressure drop over the loop had not increased with respect to the situation prior to shut-down.

TYPE C EXPERIMENTS

Experiments were carried out to measure biodegradation of quaternary ammonium compounds relevant to the present invention.

Closed bottle tests with natural sea water in accordance with the test protocol of OECD 306 revealed that the biodegradation of dibutyldicocoylammoniumbromide

remained at 0% after 28 days and that biodegradation of dimyristylester of dibutyldiethanolammonium when present in the following concentrations in sea water took place at the following rates:

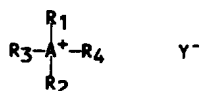
concentration (mg/l seawater)	biodegradation			
	after 5 days	after 15 days	after 28 days	after 56 days
0.42	35%	33%	50%	52-59%
1.17	37%	38%	52%	35-52%

5 On the basis of data reported in the article
"Environmental fate and effects of DEEDMAC, a new rapidly
biodegradable cationic surfactant for use in fabric
softeners" published by S.T. Giolando, R.A. Rapapart,
R.J. Larson and T.W. Federle in the magazine Chemosphere,
10 Vol. 30, No. 6, January 1995, pag. 1057-1083 about the
biodegradability of chemical compositions it can be
assumed that the diester compounds identified in the
specification will have a biodegradability which is in
line with the rates of biodegradation identified in the
15 table.

C L A I M S

1. A method for inhibiting the plugging of a conduit, the conduit containing a flowing mixture comprising an amount of hydrocarbons having from one to eight carbon atoms and an amount of water wherein the amounts of hydrocarbons and water could form hydrates at conduit temperatures and pressures, the method comprising the steps of:

adding to the mixture an amount of a hydrate formation inhibitor component of the formula



wherein two of R_1 - R_4 are independently normal or branched alkyls having 4 or 5 carbon atoms, two of R_1 - R_4 are independently representing organic moieties having at least 8 carbon atoms,

A represents a nitrogen or phosphorus atom, and

Y represents an anion,

the amount of the hydrate formation inhibitor component being effective to inhibit formation of hydrates in the mixture at conduit temperatures and pressures, and

flowing the mixture containing the hydrate formation inhibitor component through the conduit.

2. The method according to claim 1, wherein two of R_1 - R_4 independently contain between 8 and 20 carbon atoms, preferably in the range 10 to 16 carbon atoms.

3. The method according to claim 1 or 2, wherein two of R_1 - R_4 contain the same number of carbon atoms, each being at least 8.

4. The method according to claim 1, wherein at least one of R_1 - R_4 contains a hetero-atom in addition to at least 8 carbon atoms.

5. The method according to claim 4, wherein two of R_1 - R_4 contain a hetero-atom in addition to at least 8 carbon atoms.

6. The method according to claim 4 or 5, wherein the hetero-atom is an oxygen or a nitrogen atom.

7. The method according to claim 6, wherein two of R_1 - R_4 independently represent a $-(CH_2-CHR_5-O)_nH$ or $-(CH_2-CHR_5-N-R_6)_m-CH_2-CH_3$ moiety wherein R_5 represents H or CH_3 , R_6 represents H or alkyl, such as CH_3 or C_2H_5 , n represents an integer from 4 to 50 and m represents an integer from 3-5.

8. The method according to any one of claims 4-6, wherein at least one of R_1 - R_4 represents a

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$-(CH_2-CHR_5-O)_p-(CHR_5)_q-O-C-R_7$ moiety, wherein R_5 is H or CH_3 , p represents 0 or an integer up to 50, q represents an integer up to 20 and R_7 represents an alkyl, alkenyl, aryl, arylalkyl, arylalkenyl, alkylaryl or alkenylaryl group having at least a carbon chain of 6 atoms.

9. The method according to claim 8, wherein q represents 2-4 and R_7 represents an alkyl or alkenyl group having at least 9 carbon atoms.

10. The method according to claim 9, wherein p is zero, q represents 2 and R_7 represents an alkyl or alkenyl group of between 9 and 18 carbon atoms.

11. The method according to claim 10, wherein R_7 represents the carbon chain of coconut fatty acid or tallow fatty acid.

12. The method according to one or more of claims 1-11, wherein the anion represents a hydroxide, a carboxylate, a halide, a sulphate or an organic sulphonate.

13. The method according to one or more of claims 1-12, wherein between 0.05 and 11 wt%, based on the water content, of the hydrate formation inhibitor is added to the hydrocarbon/water mixture.

5 14. The method according to claim 13, wherein the amount of hydrate formation inhibitor added is between 0.1 and 5 wt%, preferably 0.1 to 0.5 wt% based on the water content.

10 15. The method according to one or more of claims 1-14, wherein a corrosion inhibitor is added to the hydrocarbon/water mixture.

15 16. The method according to claim 15, wherein the corrosion inhibitor is a primary, secondary or tertiary amine or a quaternary ammonium salt, preferably containing at least one hydrophobic group.

17. The method according to claim 16, wherein the corrosion inhibitor is a benzalkonium halide, preferably benzylhexyl dimethyl ammonium chloride.

20 18. The method according to one or more of claims 1-17, wherein a polymer of an ethylenically unsaturated N-heterocyclic carbonyl compound is added to the hydrocarbon/water mixture.

25 19. The method according to claim 18, wherein the polymer is an aliphatic (N-heterocyclic carbonyl)polymer with units derived from N-vinyl pyrrolid-2-one and an unsaturated hydrocarbon having between 4 and 30 carbon atoms.

30 20. The method according to claim 19, wherein the polymer unit is derived from N-vinylpyrrolid-2-one and butylene, octylene, dodecylene, hexadecylene, eicosylene and tricosylene.

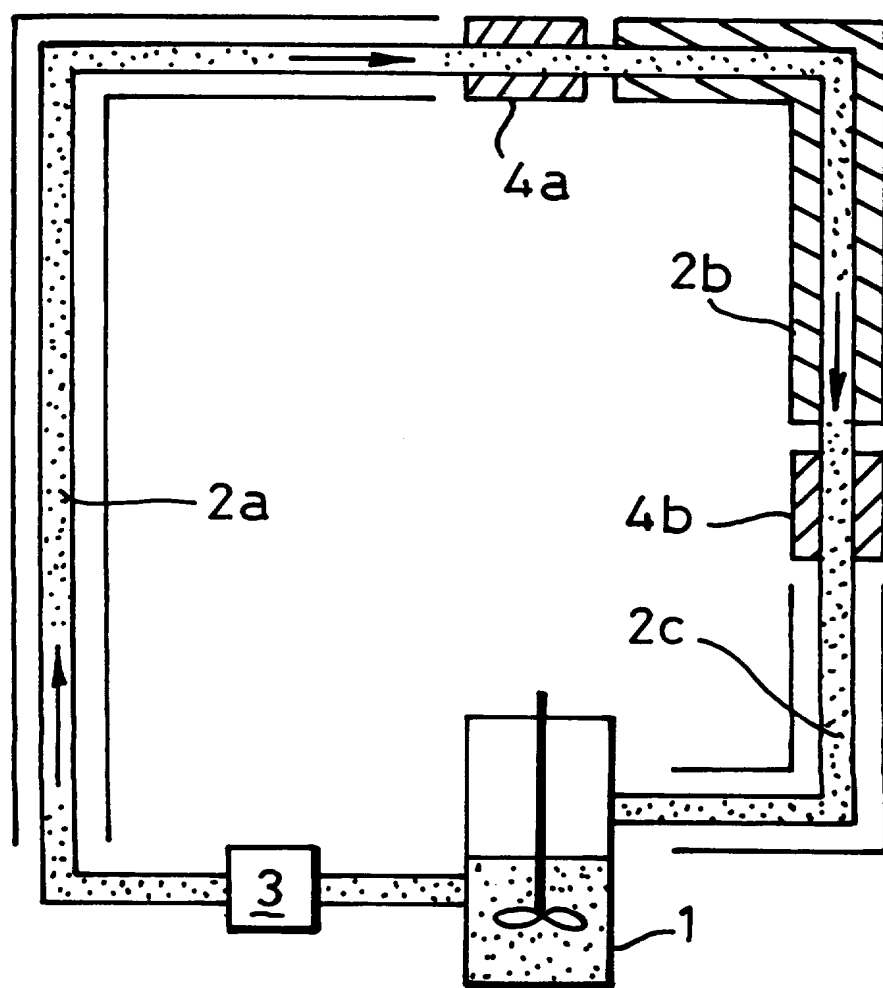


FIG. 1

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 96/01732

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 E21B37/06 C10L3/00 F17D1/02 F15D1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 E21B C10L F17D F15D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO,A,95 17579 (SHELL) 29 June 1995 see page 13; claims 1-17 ---	1,12-14, 18
P,X	WO,A,95 19408 (BP) 20 July 1995 see page 5 see page 13, line 5 - line 11 ---	1-3, 12-14, 18-20
X	WO,A,94 24413 (BP) 27 October 1994 see page 9 see page 11 ---	1-3, 12-14,18
A	WO,A,93 25798 (SHELL) 23 December 1993 cited in the application see claim 5 ---	18-20
-/-		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

8 August 1996

Date of mailing of the international search report

23.08.96

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Authorized officer

De La Morinerie, B

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 96/01732

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 96/01732

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WO-A-9519408	20-07-95	NONE	
WO-A-9424413	27-10-94	NONE	
WO-A-9325798	23-12-93	AU-B- 4325993	04-01-94
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